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(54) Process for the preparation of salt granulates.

(57) Described is a process for the preparation of salt granulates which can be used as carrier media for liquid washing agent raw materials in detergent compositions of high bulk density. The process comprises granulation under pressure of salt powder having a content of water of crystallisation of at least 10% and an average particle size of 1 to 500 µm, and subsequent extraction of the water of crystallisation in a fluidised bed at a temperature of the bed which is below the melting point of the granulate. In the granulation process use is preferably made of a mixture of water of crystallisation-holding salts and anhydrous salts.

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The invention relates to salts in the form of porous granulates, the preparation thereof, and the use thereof as carrier media for active substances, e.g. liquid washing agent raw materials, such as are put to use in detergent compositions, e.g. in washing agents, but above all in detergent compositions with a high bulk density.

The preparation of salts in the form of porous particles as well as the use thereof as carrier media for detergents has, in itself, been known for a long time. Thus, in EP-OS 221 776 a process is described which comprises drying an aqueous slurry of sodium carbonate together with detergents to form a powder. This process additionally requires the use of crystal builders. Used as crystal builders are polymeric substances, such as polyacrylates, the molecular weight of which can extend up to the order of 250 000. During drying, which preferably takes place according to the spray-drying process, powders are formed which have a comparatively wide particle size distribution spectrum. The opportunity for influencing the granule size is very limited; it is virtually impossible to prepare particles having a size in excess of 300 µm in this manner. Particles of varying particle size will absorb active substances varyingly, so that particles of varying density are formed. In handling, such as transporting or packing, this can lead to separation of mixtures, resulting in inhomogeneities and, e.g., layers of varying concentration within a single package or a concentration which varies from package to package.

In DE-OS 2 642 035 a process is disclosed which comprises blowing silicate having water of crystallisation and a stabiliser by evaporating off the water of crystallisation. In this way a product is formed with a low bulk density and particles of greatly varying particle size and a very wide pore spectrum with, in part, very large pores not suited to taking up detergents, since these will ooze out again very easily. As during the swelling process the product is very sticky, there must be a layer of stabiliser on the carrier, to prevent sticking. The processing temperatures are relatively high. Also these granulates have a tendency to separation of mixture.

In GB Patent Application 2 919 035 the preparation of granulates, more particularly alkali silicate- and/or alkali phosphate-containing granulates is described, in which process a mixture of water-containing or water-releasing material is heated in a granulating apparatus to a temperature below its melting point. As the Examples prove, in this process the water content of the material is only reduced by the order of 10%. Also, the granulates have a very wide particle size distribution, so that sieving is recommended and larger granulates have to be fed to a milling process.

Finally, in DE-PS 3 814 274 the preparation of active sodium carbonate which is more or less pulverulent is described. The particles having a granule size of 0,25 to 0,33 mm serve to remove sulphur dioxide from waste gases. To activate the sodium carbonate the water of crystallisation is gradually extracted from it, which drying process may be carried out in a fluidised bed. According to the teachings of this patent, porous granulates, which are especially suited to taking up detergents, are not obtained.

Although a whole series of processes for the preparation of porous salt granulates is already known, there is still a need for improved processes by means of which it is possible to prepare such granulates having good or improved properties. It is the object of the invention to provide a process for the preparation of salts in the form of porous granulates that works economically, is easy to be carried out, has no dust formation or only very little, and leads to granulates which are homogeneous, show no tendency to separate in either the loaded or the unloaded state, and which are, above all, utilisable as carrier media for liquid washing powder raw materials in detergent compositions of high bulk density.

This objective is attained by a process for the preparation of solid, porous, water-soluble salt granulates according to claim 1. Preferably the content of water of crystallization is at least 30%.
It is preferred that pulverulent salts holding water of crystallisation and having an average particle size of 1 to 500 µm and anhydrous pulverulent salts having an average particle size of 1 to 500 µm are intimately admixed and processed under pressure to form granulates with an average granule size of 0,300 to 3 mm, and that the water of crystallisation is then extracted wholly or in part from the granulates in a fluidised bed at a temperature of the bed which is below the melting point of the granulate. Preferably, the anhydrous salt used is sodium carbonate. Particularly suitable as water of hydration-holding salt is sodium carbonate monohydrate or sodium carbonate decahydrate, also sodium sulphate decahydrate. For the granulation process use is made with advantage of a compacting granulator; a high-shear mixer is also highly suitable.

In a preferred embodiment of the invention the mixtures of salts are mixtures of technical salts and/or raw material salts.

The granulates prepared according to the invention are especially suitable for use as carrier media for liquid washing agent raw materials in detergent compositions, more particularly in those which have a bulk density of 700 to 1100 kg/m^3, preferably 900 to 1000 kg/m^3.

According to the invention there may be processed conventional salts, pure salts, technical salts coming from industrial processes, raw material salts, more particularly soda, sodium sulphate, trona salt

($Na_2CO_3.NaHCO_3.2H_2O$), and so on, but also corresponding borates, perborates, nitrates, phosphates, and the like.

For granulation under pressure the usual processes in which pressure granulators are employed may serve. As pressure granulators within the meaning of the invention may be counted compact granulators as they have been described, int. al., in Chapter 5 of C.E. Capes's Particle Size Enlargement, Elsevier Scientific Publ. Company, Amsterdam, 1980. Also to be numbered among these are high-shear mixers, as are mentioned, int. al., in European Patent Specification 0 376 360 on p. 3, l. 55 to p. 4, l. 19. By liquid washing agent raw materials are meant conventional detergents, substances with surface active properties, additives, but also surface inactive materials, such as perfumes, and the like.

The invention will be further illustrated with reference to the following examples.

Example 1

$Na_2SO_4.10H_2O$, i.e. sodium sulphate manufactured by Riedel de Haen, No. 13571, was sized through a 1 mm screen. 1,7 kg of the sized material were granulated on a type WP 50 N/75 roller press ex Alexanderwerk and pulverised with a crusher. A screen size of 1,25 mm was selected. The pulverised material was next sized at 0,22 mm. The yield of granulate having a granule size in the range of 0,2 to 1,25 mm was 86%.

Samples of granulated product and of non-granulated but sized product were dehydrated in a Büchi 710 fluidised bed dryer. The treatment data and the properties of the obtained products are compiled in Table 1.

Table 1

Material	Glauber salt 0,20 - 1,2 mm	
Treatment	granulated	not granulated
dry air, temperature °C	65	65
throughput m³/h	38	38
product input		
matter g	150	200
volume ml	200	260
fluidised bed temp. °C	31	29
drying time min.	20	25
exhaust air, relative humidity %	42	45
throughput	*	
matter g	68	86
volume ml	160	190
porosity ml/kg	600	500

* the product was virtually anhydrous

Examples 2 and 3

In a ratio of 80 to 20 parts soda $Na_2CO_3.10H_2O$ and anhydrous sodium carbonate were intimately admixed in a 2 l Nauta mixer, granulated on an Alexanderwerk type WP 50 N/75 roller press compacting granulator at a roller pressure of 80 bar, pulverised with a crusher set at 1,6 mm, and sized at ≥ 0,4 mm. The proportion of granulate having a particle size of greater than 0,4 mm was 85%. After a treatment in the same fluidised bed dryer as in Example 1 a product of high porosity and absorptive capacity was obtained.

Further details can be taken from Table 2.

Table 2

Example	2	3
dry air, temperature °C	65	85
throughput m^3/h	38	38
product input		
matter g	200	200
volume ml	260	270
fluidised bed temp. °C	27	29
drying time min.	26	18
exhaust air		
relative humidity %	40	55
throughput		
matter g	97,5	92,3
volume ml	260	270
porosity ml/kg	545	530

Examples 4 and 5

Trona and $NaHCO_3$ as precursors

Sodium carbonate granules along the lines of examples 2 and 3 were prepared from TRONA (sodium sesquicarbonate $Na_2CO_3.NaHCO_3.2H_2O$ and from $NaHCO_3$. The temperature of the dry air was increased to 115 °C. Further details can be taken from table 3.

Table 3

Example	4	5
Precursor	Trona	$NaHCO_3$
Supplier	Solvay	M & W
Loss on ignition %	30	39
Dewatering		
t dry air °C	115	115
time min	60	60
Granules		
bulk density kg/m^3	700	700
porosity ml/kg	325	340

The porosity in the granules is not only caused by the release of H_2O as in the examples 1 - 3, but also improved by the release of H_2O and CO_2.

Example 6 and 7

Sodium carbonate granules from Solvay process streams

The novel process is also of great value when the filtercake of $NaHCO_3$, being an intermediate in the Solvay process, is used. A cake from a production plant with composition: $NaHCO_3$ = 77%, Na_2CO_3 = 6%, H_2O = 15% and NH_4HCO_3 = 2%, is used.

The filtercake has to be converted into a dry powder when compaction granulation is applied and into a crumbly powder when high shear mixer granulation is applied as the process of particle size enlargement. Such a powder of reduced free water moisture content could be obtained via a drying step, but the admixing with a calcined soda ash is preferred. The following compositions with minimum level of dry Na_2CO_3 were determined:

Consistency *	$NaHCO_3$ filtercake	Na_2CO_3
Crumbly	80	20
dry	70	30

* a standard mixing time of 15 min was applied.

Two batches of about 2 kg were prepared by mixing in the Lödige 5 l plough share mixer during 15 min. The resulting powdery mixtures were compaction granulated as described in the other examples. Details on composition drying conditions and product properties are given in table 4.

Table 4

Compsition		
$NaHCO_3$, filtercake	67	50
Na_2CO_3, light	33	50
Granulation		
Alexanderwerk, pressure in bar	80	80
Screening		
Top screen mm	1.6	1.6
Bottom screen mm	0.2	0.2
Fluid bed drying		
Temperature °C	115	115
Time min	50	60
Product properties		
Bulk density kg/m³	630	830
Porosity ml/kg	410	240

Example 8 and 9

Sodium perborate monohydrate granules

Granular perborate monohydrate is subject of two recent patent applications:

Company	No	Priority date
Degussa	DE 39 41 851	89-12-19
Peroxid-Chemie	AU 91 82 444	90-08-16

The applicants apply basically the following process:
- first step: dehydration

– second step: particle size enlargement via compaction granulation
The sodium perborate tetrahydrate used in examples 8 and 9 is part of: IEC Test Detergent with Perborate, manufactured and packed by Henkel KGaA, July 1987. The compaction granulation went along the lines of previous examples. The dehydrated products are compared in table 5.

Table 5

Example	8	9
Feed: type	crystals	granules
amount g	90	90
Drying:max temp °C	70	70
Conditions:air m^3/h	40	40
time min	45	45
Bed:max temp °C	60	60
Product dust in filterbag g	4	<0.5
Output g	61	65
Active oxygen %	14.6	14.7
Bulk density kg/m^3	470	640
Porosity ml/kg	420	280

The key advantage of the novel route is that the safety risk from the dust which is formed by drying is clearly reduced. What is more the granules are appropriate to prepare super compact detergent via the concept of filling pores in a carrier by liquid ingredients. The bulk densities which are expected upon sorption of a liquid with density 1000 kg/m^3 is given in the table 6.

Table 6

Comparison of the two carriers		
	Crystal	Granules
1 m^3 of carrier kg	470	640
Porosity l	197	179
Liquid adsorbed kg	197	179
Final bulk density kg/m^3	567	819

Example 10

Porous granules based on particle size enlargement by high shear mixing.
Na_2CO_3 granules with about 2.5 mol of H_2O were made in the 40 l high shear mixer of Diosna.
The following procedure was found as optimum.

Time in sec	Action
0	To fill with 5.0 kg soda ash light
0 – 10	To add 2.0 kg of water at speed impeller M 1 and chopper 2
10 – 30	To continue mixing
30 – 45	To change speed from M 1 to M 2
45 – 50	To admix 0.5 kg soda ash light
50 – 60	To empty the bowl

The sticky granules were spread onto trays. The granules cooled down and hardened in about one hour.

The granules were screened to obtain the size fraction 0.2 – 1.6 mm. This fraction was dried in the fluid bed drier at 116 °C. We determined the following properties:

Bulk density	700 kg/m^3
Porosity	240ml/kg

Example 11 – 14

Drying with Torbed® process

Fluidised beds have been used in the industry for many years and the technology to optimise their use has been under constant study throughout that time. It is referred to C.M. van't Land, Industrial drying equipment, selection and application, 1992 Marcel Dekker. The Torbed® process is a recent design (US 4 479 920) not included in the review book.

Particles to be processed are moved into a toroidal way above a circle of supporting vanes upon blowing gas trough the chinks between the vanes.

The Torbed® process is commerciallized now by Davy McKee, Stockton-on-Tees, England. We applied the following test conditions:

Type of equipment:	T 400
Open surface:	15%
Type of operation:	batch
Collection of fines:	cyclone
Collection of product dust:	grit trap
Generation of drying air:	direct fired with gas

The feed for the drier (green granules) were prepared from the Solvay process streams $NaHCO_3$ filtercake and calcined soda ash. The two test compositions of examples 6 and 7 were extended to four. The mixing step got upscaled now to the 50 l plough share mixer, made Drais.

The powder from example 14, having the highest content of $NaHCO_3$ filtercake was crumbly of character with as a consistency borderline processibility in the next compaction granulation step.

Upon mixing $NaHCO_3$ filtercake and Na_2CO_3 an exothermic reaction starts. IR analysis showed the formation of sodium sesquicarbonate (= Trona, $Na_2CO_3.NaHCO_3.2H_2O$) while the component having the smallest mol fraction completely disappears in the IR-spectrum.

The survey of the process conditions which we applied is given in table 6.

Most striking is that the drying time is reduced by a factor 10 when using the latest fluidised bed development while the product properties look similar.

Most is more, the temperature recorder indicated that the drying process of the green granules comprising Trona and $NaHCO_3$ is a two step process: The fast step is the most endothermic (0-1 min) followed by slower less endothermic step (1-3 min). This observation makes the installation of a Torbed device with more drying circles attractive. The heat economy will increase consequently. The CO_2 content of the flue gas will increase, easying the recycle step in the Solvay absorbing tower.

Table 6

Example		11	12	13	14
Composition	$NaHCO_3$ cake %	51	59	67	75
	Na_2CO_3 %	49	41	33	25
Mixing	Feed kg	22	19	22	15
	Feed temp °C	22	22	22	22
	T max °C	46	53	60	56
Compaction granulation	Pressure bar	80	80	80	80
	Throughput kg/h	70	71	84	71
	Yield % on.3-1.6 mm	73	75	82	80
Green granules	Bulk Density kg/m³	940	920	925	960
	Loss on ignition %	25.4	29.1	33.1	36.5
Drying step Torbed	Temp.gas °C	200	200	200	200
	Time min	3	3	3	3
	Input g	674	636	637	660
	Output* 9	283	276	268	241
	Cyclone*	8	37	10	24
Absorbent granules	Bulk Density kg/m³	735	685	645	602
	Porosity ml/kg	305	345	370	380
	Loss on ignition %	0.6	0.5	0.5	0.6

* average of three batches

Uses of porous salt granules

The granules prepared according to the invention are especially suitable for use as carrier media for liquid washing ingredients. The impregnated carriers are specially suitable for blending into detergent compositions with a bulk density of 700 to 1100 kg/m³, preferable 900 to 1000 kg/m³.

By liquid washing ingredients are meant conventional detergents, substances with surface active properties but also surface inactive materials.

Examples of the resulting delivery systems are given:

- parfume granule
- anti foam granule

It was found that the antifoam liquid of Dow corning, coded B-3332, comprising 95% silicone oil and 5% silica was easily impregnated without any formation of a silica skin at the outer surface.

- enzyme active granule

A dispersion of enzymes in liquid nonionics like Elfapur LT 85® or liquid polyethylene glycol is easily impregnated into the carriers of this process.

- activator formulation via absorption of liquid or dissolved activator.
- disinfactant granule by combining the sorbentia and a disinfecting cationic active material like Arquad B 80®.

Analytical procedures employed in the examples.

1. Bulk density: Method DIN 53912
2. Porosity:

The total porosity of carriers is based on the sorption of a liquid (2-propanol). The carrier is oversaturated first followed by removal of the surplus of liquid by a centrifugal step. The method is described in detail by Daniel McM and Hottovy T: J. of Coll. and I Sc., 78 November 1980, 31. It was confirmed that liquid nonionic loaded till this porosity value on a carrier will not ooze to carton upon contact.

Claims

1. A process for the preparation of solid, porous water-soluble salt granulates, characterised in that powder or powder mixtures of salts having a content of water of crystallisation of at least 10% and an average particle size of 1 to 500 µm are processed under pressure to form granulates having an average granule size of 0,300 to 3 mm, and the water of crystallisation is extracted wholly or in part from the granulate in a fluidised bed at a temperature of the bed which is below the melting point of the granulate.

2. A process according to claim 1, characterised in that the content of water of crystallisation is at least 30%

3. A process according to claim 1 or 2, characterised in that pulverulent salts holding water of crystallisation and having an average particle size of 1 to 500 µm and pulverulent anhydrous salts having an average particle size of 1 to 500 µm are intimately admixed and processed under pressure to form granulates with an average granule size of 0,300 to 3 mm, and the water of crystallisation is extracted wholly or in part from the granulates in a fluidised bed at a temperature of the bed which is below the melting point of the granulate.

4. A process according to claim 3, characterised in that the anhydrous salt used is sodium carbonate.

5. A process according to any one of claims 1-4, characterised in that the water of crystallisation-holding salt is sodium carbonate monohydrate or sodium carbonate decahydrate.

6. A process according to any one of claims 1-4, characterised in that the water of crystallisation-holding salt used is sodium sulphate decahydrate.

7. A process according to any one of claims 1-4, characterised in that the water of crystallisation-holding salt used is trona salt.

8. A process according to any one of claims 1-4, characterised in that the water of crustallysation used is sodium perborate tetrahydrate.

9. A process according to one or more of claims 1-8, characterised in that for the granulation process use is made of a compacting granulator.

10. A process according to one or more of claims 1-8, characterised in that for the granulation process use is made of a high-shear mixer.

11. A process according to one or more of claims 1-10, characterised in that the mixtures of salt are mixtures of technical raw materials.

12. Use of the granulates prepared according to one or more of claims 1-11 in detergent compositions as carrier media for liquid washing powder raw materials.

13. Use according to claim 12 in detergent compositions having a bulk density of 700 to 1100 kg/m^3.

14. Use according to claim 13, characterised in that the bulk density is 900 to 1000 kg/m^3.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 20 3402

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	BE-A-779 149 (UZINA DE PRODUCE SODICE) * the whole document * ---	1,5,9	C11D17/06
A	FR-A-2 224 407 (SOLVAY & CIE,) * the whole document * ---	1-5,9,12	
A	DE-C-925 773 (DEUTSCHE SOLVAY-WERKE GMBH.) ---		
A	US-A-4 001 381 (A.M. DASCALESCU ET AL.) -----		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C11D
B01J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	09 FEBRUARY 1993	PYFFEROEN K.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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